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COMPLEX ADDITIVE TO ACID ELECTROLYTES FOR PRODUCING COMPOSITE
COATINGS BASED ON NICKEL AND NICKEL-COBALT ALLOY
[KOMPLEKSNAYA DOBAVKA V KISLYYE ELEKTROLITY Dlya POLUCHENIYA
KOMPOZITSIONNYKH POKRYTIY NA OSNOVE NIKELYA AND SPLAVA NIKEl'-
KOBAL'T]

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Complex additive to acid electrolytes for producing composite coatings based on nickel and nickel-cobalt alloy

The invention pertains to electroplating, to the application of composite electro-chemical coatings in particular, and it can also be used in the automobile, tool, machine-building and other branches of industry where hard and wear-resistant protective and decorative coatings are needed.

The goal of the invention is to increase the hardness of composite coatings.

The coating is made in electrolytes that contain a complex additive in the form of methyl cellulose and betaine 2-(4-pyridyl)-ethanesulfonic acid. The composite electro-chemical coatings are made with current density of 5-8 A/dm² and temperature 45-50°C.

The combined use of betaines 2-(4-pyridyl)-ethanesulfonic acid and methyl cellulose promotes the production of good quality thick-layer composite electro-chemical coatings with excellent micro-hardness (700-850 kgf/mm²) and content of non-metallic micro-powders (6-20% by volume), including maximum concentrations of supplemental additives. The additive has a twofold effect: not only does it increase the hardness of the composite

¹ Numbers in the margin indicate pagination in the foreign text.

electro-chemical coatings and stimulate the co-precipitation of powders with metal, but it promotes the production of high-quality thick-layer coatings. It changes the surface properties of the powder and affects the grain size of the metal structure, and therefore hard coatings with high powder content are produced. The

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additive also improves the sedimentation stability of the powder in the electrolyte.

Example 1. 20.92 g of 2-(4-pyridyl)-ethanesulfonic acid and 4 g of sodium hydroxide are dissolved in 100 ml of water, 8.04 g of ethylene chlorohydrin and it is boiled with a reflux condenser for 16 hours. Next the solution is boiled down in vacuum, the dry residue is dissolved in 100 ml of cold concentrated HCl. The undissolved sodium chloride is filtered out through a glass filter, the filtrate is concentrated by evaporation in a vacuum. The residue is re-crystallized from a mixture of ethanol and water (3:1). 18.77 g of product are obtained, yield 81.2%, melting point approximately 218°C (variable).

Calculated: %: C 46.74; H 5.66; S 13.86.

C₄H₁₃N₀4S.

Found, %: C 46.89, 46.76; H 5.66, 5.83; S 13.89, 13.66.

Example 2. In a similar manner, from 10.46 g of 2-(4-pyridyl)-ethanesulfonic acid, 2

g of sodium hydroxide in 50 ml of water and 5.52 g of alpha-monochlorohydrin glycerine we get 12.13 g of product, yield 92.9%, and it is re-crystallized from a mixture of ethanol and water (2:1); melting point approximately 239°C (variable).

Calculated, %: C 45.96; H 5.78; S 12.27.

C₁₀H₁₅N₀S₅.

Found: percentage by weight: C 45.63, 45.60; H 5.88, 5.71; S 13.02, 11.69.

Example 3. To a solution of 9.36 g of 2-(4-pyridyl)-ethanesulfonic acid in 50 ml of water we added 3.6 g of acrylic acid and 0.1 ml of triethylamine. The resulting reaction mixture is boiled for 16 hours, next it is boiled down in a vacuum. The residue is re-crystallized from ethyl alcohol. 9.9 g of product are produced with yield of 76.4%, melting point approximately 254°C (variable).

Calculated, %: C 46.32; H 5.05; S 12.36.

C₁₀H₁₃N₀S₅.

Found, %: C 46.03, 46.37; H 5.12, 5.03; S 12.03, 12.45.

Example 4. 10.46 g of sodium salt of 2-(4-pyridyl)-ethanesulfonic acid are dissolved in 50 ml of water, a few drops of alcohol solution of phenolphthalein solution and 4.63 g of epichlorohydrin are added. The mixture is vigorously stirred at room temperature and

at the appearance of a reddish violet color diluted (approximately 2N) hydrochloric acid is added gradually. The addition of acid is carried out at such a rate that the reaction mixture does not acquire a deep coloring. When the reaction slows down the temperature is raised to 40-50°C. After the end of the reaction 7.46 g of triethanolamine is added and it is boiled with reflux condenser for 16 hours. Next the water is concentrated by evaporation until dry with a rotary evaporator and the residue is extracted by boiling ethyl alcohol (3 X 200 ml). The crystals that form during cooling are filtered out and dried in a vacuum drying unit. 15.75 g are produced, yield 73.4%, and it is re-crystallized from ethyl alcohol.

Calculated, %: N 6.53.

C₁₆H₂₉ClN₂O₇S.

Found, %: N 6.92, 7.10.

The structure of the synthesized compounds was confirmed by infrared and ultraviolet spectra data. The methyl cellulose is made by industry. The electrolyte additive is added in the following manner.

Initially, one prepares a sulfuric acid or sulfamic acid nickel plating electrolyte or an electrolyte for precipitation of Ni-Co alloy of known composition (examples are

given in the table). It is purified with activated charcoal and selectively purified. The required amount of micro-powder, which is mixed with a small amount of purified electrolyte, is weighed in a separate container. To the resulting pasty mass one adds the required amount of solution of methyl cellulose and betaine 2-(4-pyridyl)-ethanesulfonic acid; the mixture is stirred thoroughly and after a 20-minute interval the given mixture is transferred to a bath, which contains the required amount of electrolyte. Stirring of the electrolyte suspensions are carried out with compressed air.

Commercial micro-powders are used: green silicon carbide (KZ) with M5 fineness (basic fraction 3-5 mcm), white manufactured corundum EB M3 (basic fraction 1-3 mcm), manufactured corundum M1, boron nitride beta (elbor) M3. The size of the particles of manufactured corundum used should not exceed 20 mcm, and its concentration in the electrolyte can be 50-300 g/l.

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The specific examples, which illustrate the use of the additive, are given in the table.

As one can see from the table, the additive offers the opportunity to produce composite electro-chemical coatings with varying non-metallic micro-powders: carbides,

oxides, nitrides and boron. The additive can be used to produce self-lubricating composite coatings. For example, high quality coatings that contain 12 % by volume of inclusions can be produced with graphite micro-powder.

Analysis of the examples presented here shows that the concentration of betaines 2-(4-pyridyl)-ethanesulfonic acid can be increased up to 1.5 g/l (example 12) without harm to the quality of the resulting composite electro-chemical coatings. The resulting coatings have high percentage of inclusions and excellent micro-hardness (20.8% by volume and 890 kgf/mm² respectively). However, increasing the additive concentration above the indicated limit can lead to cracking of the composite electro-chemical coatings. The maximum concentration of methyl cellulose is limited by the fact that its high quantities negatively affect the co-precipitation of powder (example 11), although in this case a most stable suspension is formed.

With the addition of betaines 2-(4-pyridyl)-ethanesulfonic acid of less than 0.25 g/l composite electro-chemical coatings are produced, whose micro-hardness is not high. Thus, in order to produce hard composite electro-chemical coatings the additive concentration must be kept in the range of 0.3-1.2 g/l. A wide range of working concentrations of additive is an important property of the electrolyte for the production of thick layers.

CLAIMS

1. A complex additive for acid electrolytes for the production of composite coatings based on nickel and nickel-cobalt alloy that includes a nitrogen-containing compound, is characterized in that in order to increase the hardness of coatings, it additionally contains methyl cellulose, and as the nitrogen-containing heterocyclic compound betaine 2-(4-pyridyl)-ethanesulfonic acid with the general formula:

R₂R₁CH-CH₂-+NC₆H₄-CH₂-CH₂SO₃, where R₁ is H or -OH;

R₂-OH₁-CH₂OH,

-COOH, -CH₂N(CH₂CH₂O)₃Cl,

With the following ratio of ingredients, g/l:

- Methyl cellulose 0.15-2.0
- Betaine 2-(4-pyridyl)-ethanesulfonic acid 0.3-1.5.

TABLE

Composition of electrolyte,	Example												
	1 basic	2 known	3	4	5	6	7	8	9	10	11	12	13

<i>g/l,</i> precipitation conditions and properties of the composite electro- chemical coatings												
nickel sulfate (hydrate)	100	100	300	300	240	240	300	300	240	-	300	320
nickel [illegible]	-									400		
nickel chloride	45	45	45	45	45	45	40	40	40	25	45	45
(hydrate)											40	
cobalt sulfate (hydrate)	-								-25			
boric acid	30	30	30	30	30	30	30	30	30	40	40	40
silicon	100	100	100	150					100		200	300
carbide K3 M5												150
synthetic corundum EB												
M10							100					

synthetic												
corundum EB M3									100			
boron nitride				75								
alpha (16 mcm)												
synthetic												
corundum M3					50							
amorphous												
boron							50					
methyl violet	0.2											
betaines 2-(4-												
(pyridyl)-												
ethanesulfonic												
acid		0.4	0.8	0.6	0.5	0.5	0.3	0.6	1.0	0.2	1.5	0.6
methyl												
cellulose		0.3	0.4	1.2	0.5	0.15	0.4	0.8	0.6	2.5	0.5	2.0
cathode												
current												
density, A/dm ²	5	5	5	6	7	4	5	7	8	7	5	5
pH of												
electrolyte	4	4	4	4	4	4	4	4	4	3.6	3.6	4
electrolyte												
temperature,												
°C	45	45	45	45	45	50	50	50	45	50	45	45

coating thickness, mcm	50	50	50	150	50	50	250	50	50	50	50	100	50
content of micro-powder inclusions, percent by volume	1.5	13.2	15.0	12.7	6.3	10.5	13.7	16.0	13.0	13.5	2.8	20.8	4.5
microhardness, kgf/mm ²	280	630											
suspension stability (3 cm sedimentation time), min	16	9											
internal stresses kgf/cm ²	790	1420											
plasticity, %	4.2	1											

Note: The current efficiency in all cases is 94-98%; the rate of precipitation at

5 A/cm² is on the order of 1 mcm/min; the dispersion factor according to the Herckel-Klug method is 24-26%; the coatings can have thicknesses of 1000 mcm or more.